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The nature of the interaction of organoselenium molecules with diiodine

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Abstract

The electronic structure of charge-transfer complexes of organoselenium compounds with diiodine has been studied at several levels of theory (Hartree-Fock, second order Møller-Plesset, and density functional theory). The complexation energies, optimized geometries, and the topology of the electron density and its Laplacian distribution, including domain averaged properties, have been analyzed. Special attention was paid to the influence of basis set superposition error on the energy of complexation. A tendency of organoselenium molecules to form more covalent intermolecular bonds with electron acceptors than with nitrogen atoms or other conventional electron donors has been revealed. The changes in atomic charges under complexation follow the main trends expected for the charge transfer. By means of the interacting quantum atoms (IQA) approach it has been found that the Se···I interaction is dominated by its quantum mechanical exchange-correlation contribution, the electrostatic interaction having a minor, repulsive role. IQA data have also been used to explain the value of the Se···I-I valence angle, as well as the topological charges on the iodine atoms in the complexes studied. © 2011 American Chemical Society.

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